

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PATENT SPECIFICATION

(11) 1 464 198

1 464 198

- (21) Application N. 35576/75 (22) Filed 28 Aug. 1975
 (31) Convention Application No. 522392 (32) Filed 11 Nov. 1974 in
 (33) United States of America (US)
 (44) Complete Specification published 9 Feb. 1977
 (51) INT. CL.² C07D 307/60 B01J 27/28
 (52) Index at acceptance



C2C 215 247 253 25Y 296 297 305 30Y 351 352 369 386
 409-40Y 410 411 412 413 414 418 419 41Y 46Y
 635 761 TQ
 B1E 277 280 306 371 37Y 383 38Y 420 42Y 463 61X
 651 75X 75Y

(54) REGENERATION OF VANADIUM-PHOSPHORUS CATALYST COMPLEX WITH ALKYL PHOSPHATES

(71) We, MOBIL OIL CORPORATION, a corporation organized under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention is concerned with *in situ* regeneration of vanadium - phosphorus - oxygen catalyst complexes used in the vapor phase oxidation of hydrocarbons to maleic anhydride.

In United States Patents No. 3,296,282 and 3,474,041, there is described a method of regenerating vanadium - phosphorus - oxygen catalysts used in the oxidation of olefins, such as butene - 2, to maleic anhydride. The method consists of treating the catalyst with a phosphine, phosphite or phosphonate by periodically or continuously passing the phosphorus compound to the reactor, with or without interrupting olefin feed flow. The patentee does not teach that esters of orthophosphoric acid are effective and prefers phosphorus compounds wherein the phosphorus has a valency of less than plus five.

United States Patent No. 2,426,678 is concerned with the regeneration of spent solid phosphate dehydration catalysts with volatile trialkyl phosphates. The patentee does not teach regeneration of vanadium - phosphorus - oxygen complex catalysts, which are not phosphate catalysts.

We have now developed a method of regenerating *in situ* a vanadium - phosphorus - oxygen catalyst complex used in the vapor phase oxidation of alkanes and/or cycloalkanes.

According to the invention, there is provided a process for the vapor phase oxidation of a feedstock consisting of or comprising one or more alkanes having from 4 to 10 carbon atoms and/or one or more cycloalkanes hav-

ing from 4 to 10 carbon atoms to form maleic anhydride, in which the feedstock is contacted in the presence of molecular oxygen with a vanadium - phosphorus - oxygen catalyst complex promoted with zirconium, hafnium, chromium, iron, lanthanum, or cerium, the catalyst being regenerated by contacting it during the vapor phase oxidation with an alkyl ester of orthophosphoric acid having the formula (RO)₃P=O, wherein R is hydrogen or C₁—C₄ alkyl, at least one R being C₁—C₄ alkyl.

The promoted catalysts that are regenerated according to this invention are prepared by refluxing a reaction mixture of vanadium oxide, phosphoric acid, a hydrogen halide (usually hydrochloric acid), and a specified promoter metal compound. In place of V₂O₅, other vanadium compounds such as VOCl₃, VO(NO₃)₃, NH₄VO₃ and VF₃ can be used. Similarly, compounds hydrolyzable to phosphoric acid can be used, such as P₂O₅ and POCl₃. The hydrogen halides are HCl, HBr and HI. Alternatively, the promoter metal compound can be added at a later stage of the catalyst preparation. For example, the promoter metal compound can be added just prior to catalyst pelletization. The proportions of reactants are selected to afford an atomic ratio of phosphorus/vanadium of between about 0.5 and about 2 and an atomic ratio of promoter metal/vanadium of between about 0.0025 and about 1, preferably between about 0.005 and about 0.5.

The optimum atomic ratio of promoter metal/V will depend upon the particular metal selected. In general, the best ratio can be found from the specific working examples of German Auslegeschrift No. 2328027, to which reference is made, or can be readily determined with a minimum of experiments.

The reaction mixture is heated at reflux temperature for from 0.5 to 24 hours, during which time the solution changes color, usually from brown to dark blue. The reaction mixture is then concentrated and evaporated to

50

55

60

65

70

75

80

85

90

dryness. The catalyst is prepared by grinding the resultant solid material to about 20-60 mesh size and pelletizing, for example, to 1/8" x 5/32" cylindrical pellets. Optionally, a binder, such as stearic acid, can be added before pelletizing. Alternatively, the reaction mixture or a concentrate thereof can be used to impregnate a suitable carrier, such as alumina or alundum, silica, silicon carbide, silica - alumina, zeolite, zirconium phosphate and/or zirconia, to produce a supported catalyst suitable for use in a fixed or fluidized bed reactor. As a further alternative, the dried catalyst (unsupported) can be ground to produce a powdered catalyst for use in a fluidized bed reactor.

In practice, the vanadium salt is added as vanadium oxychloride, which is formed by reaction *in situ* of vanadium pentoxide with hydrochloric acid. Alternatively, other oxyhalide salts of vanadium can be used, suitably prepared by reacting vanadium pentoxide with another acid such as hydrobromic or hydriodic. The phosphoric acid used generally will have a strength of between about 25 percent and about 100 percent. The promoter metal compound can be any compound of the promoter metal, such as nitrate, chloride, acetate, oxide, carbonate and the like. The promoter metals utilizable in the catalysts contemplated herein are chromium, iron, hafnium, zirconium, lanthanum and cerium. Iron and hafnium are particularly preferred for fixed bed operations, while zirconium is preferred for fluid bed operations. Zirconium generally provides a more active catalyst which provides higher yields of desired product (i.e. maleic anhydride) at lower activity temperatures in fluid bed operations. The zirconium-promoted catalysts are generally harder, such that they have improved resistance to attrition as compared with the corresponding unpromoted catalysts and with the corresponding catalysts promoted with other metals.

The feedstock used in the process according to the invention is one or more alkanes having from 4 to 10 carbon atoms and/or one or more cycloalkanes having from 4 to 10 carbon atoms; mixtures of hydrocarbons rich in alkanes and cycloalkanes having from 4 to 10 carbon atoms can also be used. The alkanes can be normal or branched. Suitable alkanes are, for example, butane, pentane, isopentane, hexane, isohexane, 3-methylpentane, heptane, octane, isooctane and decane. The cycloalkanes used can be methyl substituted and suitable cycloalkanes include, for example, cyclobutane, cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, 1,4-dimethylcyclohexane, cycloheptane, and cyclooctane. Mixtures of hydrocarbons rich in alkanes and cycloalkanes having from 4 to 10 carbon atoms, that is containing about 70 weight percent or more of such alkanes and cycloalkanes, are well known in the art. Parti-

cularly suitable and readily available mixtures are naphthas obtained from paraffinic or naphthenic petroleum sources. Full boiling range naphthas (boiling within the range of about 35-230°C.) can be used, but it is preferred to use light naphtha cuts boiling within the range of about 35-145°C. The naphthas usually contain about 5-15 weight percent benzene and alkylbenzenes. It has been found that benzene is oxidized to maleic anhydride in the process of this invention, whereas to some extent alkylbenzenes are oxidized to benzene carboxylic acids. It will be understood that other mixtures can be used, such as paraffinic raffinate from the glycol-water solvent extraction of reformates (Udex process).

Butane, because of its ready availability, is the preferred feedstock. In the following discussion and exemplification, therefore, butane is used to demonstrate (but not to limit) the present process for producing maleic anhydride and catalyst regeneration. It is contemplated that mixtures rich in butane can be used, such as a typical butane - butene-(B-B) refinery stream.

The oxidation of n-butane (or other feedstock) to maleic anhydride is carried out using air or other molecular oxygen-containing gases, such as mixtures of carbon dioxide and oxygen or mixtures of nitrogen or steam with air or oxygen. Air is preferred. The oxidation reaction is suitably carried out at a temperature of from 300 to 600°C.; preferably from 350 to 550°C. The feed concentration is preferably from 0.5 to 6 volume percent feedstock in the oxygen-containing gas and preferably 1 to 5 volume percent. Suitable contact times are from 0.08 to 3 seconds, preferably from 0.16 to 1.6 seconds for fixed bed operation. Contact times of, for example, up to 30 seconds may be used in the case of a fluidized bed operation. Thus the contact time, depending upon the type of operation, will generally be from 0.08 to 30 seconds. Although the reaction can be carried out at from 0.5 to 20 atmospheres pressure (absolute), it is preferably carried out at substantially atmospheric pressure, that is, from 1 to 7 atmospheres pressure (absolute).

The reaction can be carried out in any suitable reactor for effecting vapor phase oxidation reactions. A fixed catalyst bed may be employed or the reaction may be carried out using smaller catalyst particles in a fluidized reactor bed. A suitable fixed bed reactor consists, for example, of a 14" x 3/4" i.e. stainless steel tube equipped with a 1/4" o.d. axial thermowell for temperature measurement. A 12" portion of the reactor is encased in a brass block and temperatures are measured at the hottest point in the catalyst bed and in the brass block. Heat is supplied to the reactor through tubular electrical heaters.

In the afore-described oxidation process, the promoted vanadium - phosphorus - oxygen

catalyst begins to lose activity after a period of use. The yield of maleic anhydride drops and, in some cases, the selectivity also drops. In accordance with the invention, the catalyst is regenerated by contacting it with an alkyl ester of orthophosphonic acid while the oxidation reaction is still in progress, i.e. without interrupting the feed of hydrocarbon and oxygen.

The alkyl esters of orthophosphoric acid that are used are the mono-, di-, and trialkyl phosphates having 1-4 carbon atoms in the alkyl group. Suitable phosphoric acid esters are, for example, dimethyl hydrogen phosphate, trimethyl phosphate, ethyl dihydrogen phosphate, diethyl hydrogen phosphate, triethyl phosphate, dipropyl hydrogen phosphate, triisopropyl phosphate, butyl dihydrogen phosphate, diisobutyl hydrogen phosphate, and tributyl phosphate. Trimethyl phosphate is preferred.

The phosphate ester can be added to the catalyst by various methods, such as by addition in gaseous or liquid form. The ester can be added by use of an aerosol or in suspension in a carrier, such as steam. The phosphate ester can be introduced via the oxygen feed or the hydrocarbon feed. It has been found feasible to pass a portion of the oxygen (air) feed through a scrubber containing the phosphate ester and then introducing the air into the reactor with the rest of the air feed. The amount of phosphate ester can be controlled by the length of time the air passes through the scrubber, or by increasing or decreasing the rate of flow through the scrubber or even intermittently discontinuing the flow. The amount of alkyl ester of orthophosphoric acid added is preferably from 0.01 to 0.2 pound per pound of catalyst per year.

In order that the invention may be more fully understood, the following examples are given by way of illustration.

EXAMPLE 1

n - Butane was oxidized to maleic anhydride in a one-inch, 4 foot long glass fluid bed reactor. The catalyst was vanadium - phosphorus - zirconium catalyst (325 grams) having an atomic ratio of 1/1.2/0.13. A 4% butane in air mixture was passed through the catalyst at 400°C. Under these conditions after 386 hours of continuous reaction, the yield of maleic anhydride was 84.7% by weight at 92% butane conversion (54% selectivity). At the same conditions after 985 hours of operation, the maleic anhydride yield was 77.8% at 87.2% butane conversion (53%

selectivity). After 1200 hours of operation, a portion of the air stream (15% of the total air stream) was passed through a scrubber containing trimethyl phosphate before entering the reactor as a saturated solution of trimethyl phosphate in air. During a nineteen-hour period, a total of 0.4 g of trimethyl phosphate was added. The yield of maleic anhydride after 1320 hours was 83.3% at 81.8% butane conversion (60% selectivity).

EXAMPLE II

n - Butane was oxidized to maleic anhydride in a one-inch, 1 foot long steel fixed bed reactor. The catalyst was a vanadium - phosphorus - iron catalyst (85 grams) having an atomic ratio of 1/1.2/0.03. A 2% butane in 1:1 air-stream was passed through the catalyst at 485°C. The initial yield (48 hours) of maleic anhydride was 67.6% by weight at 68% butane conversion (59% selectivity). After 168 hours the yield of maleic anhydride dropped to 37.2% at 82% butane conversion (27% selectivity). Trimethyl phosphate was added to the reactor by passing a feed of trimethyl phosphate in steam (0.75 g trimethyl phosphate/liter of water) for one hour. A total 0.34 g of trimethyl phosphate was added to the catalyst bed during this period. After 175 hours the yield of maleic anhydride was 64.2% at 71% butane conversion (54% selectivity).

WHAT WE CLAIM IS:—

1. A process for the vapor phase oxidation of a feedstock consisting of or comprising one or more alkanes having from 4 to 10 carbon atoms and/or one or more cycloalkanes having from 4 to 10 carbon atoms to form maleic anhydride, in which the feedstock is contacted in the presence of molecular oxygen with a vanadium - phosphorus - oxygen catalyst complex promoted with zirconium, hafnium, chromium, iron lanthanum, or cerium, the catalyst being regenerated by contacting it during the vapor phase oxidation with an alkyl ester of orthophosphoric acid having the formula $(RO)_3P=O$, wherein R is hydrogen or C_1-C_4 alkyl, at least one R being C_1-C_4 alkyl.

2. A process according to claim 1, in which the alkyl ester is trimethyl phosphate.

3. A process according to claim 1 or 2, in which the amount of alkyl phosphate used is from 0.01 to 0.2 pounds per pound of catalyst per year.

4. A process according to any of claims 1 to 3, in which the feedstock consists of or comprises n - butane.

5. A process according to claim 1 substantially as herein described in either of the Examples.

5 6. Maleic anhydride produced by the process claimed in any of claims 1 to 5.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303/306 High Holborn,
London, W.C.1.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1977
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.